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<p>(54) Title: ADHESIVE FOR POLYCARBONATE</p> <p>(57) Abstract</p> <p>The invention provides radiation-cured adhesive compositions which maintain adhesion to polycarbonate surfaces. The adhesive compositions comprise a monomeric acrylic or methacrylic acid ester, a copolymerizable reinforcing monomer, a copolymerizing macromonomer and a photoinitiator.</p>		

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ADHESIVE FOR POLYCARBONATE

This application is a continuation-in-part of U.S. Serial No. 07/986,469, filed December 7, 1992, the contents of which are hereby
5 incorporated by reference.

FIELD OF THE INVENTION

This invention relates to radiation curable compositions which, when cured, yield viscoelastic polymers having improved adhesion to
10 polycarbonate surfaces after heat aging. The invention also relates to radiation cured pressure sensitive adhesives made with the composition and to tapes made with such pressure sensitive adhesives.

BACKGROUND

15 Pressure sensitive adhesives are well known in the art and are used for bonding a variety of different surfaces. However, some adhesives do not bond well to certain polymeric surfaces. Poor adhesive bonding is especially evident on high performance polymers such as polycarbonate and polyphenylene oxide. Polycarbonate is
20 particularly difficult to bond to because it is believed that the polycarbonate outgasses and causes blistering in the adhesive, which in turn, causes separation of the adhesive and the polycarbonate. The problem is even greater when the polycarbonate must withstand heat aging at elevated temperatures where a noticeable decrease in
25 peel adhesion is typically seen after heat aging with the conventional pressure sensitive adhesives.

European Patent Publications EP 353,677 and EP 304,779 describe a pressure sensitive adhesive said to be useful for bonding to polycarbonate surfaces where there is no blistering. The adhesive
30 comprises 50-85% of a first monomeric moiety of an acrylic ester, 1-30% of a second monomeric moiety of an acrylic compound having a polar group, and 5-40% by weight of a third monomeric moiety having a polymeric molecular chain and a polymerizable functional group at the end of the molecular chain. The adhesives taught in these
35 publications are solvent based.

U.S. Patent No. 4,554,324 (Husman et al.) discloses acrylate copolymer pressure sensitive adhesive compositions having A and C monomers and optionally, B monomers. The A monomers are alkyl
40 acrylate monomers, the C monomers are macromonomers, and the optional B monomers are polar monomers copolymerizable with the A monomers. While these compositions are generally prepared using solvent based copolymerization, it is stated copolymerization may also use other well known techniques such as suspension, emulsion, and bulk polymerization, but do not give any advantages of one method of

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polymerization over another. Hsuan et al. does not mention adhesion to polycarbonate.

European Patent Publication 187,044 (Kerr et al.) describes radiation curable macromonomer compositions and products. The publication describes the addition of the macromonomer to a reactive diluent which solubilizes the macromonomer. Once stabilized, the mixture is photopolymerized. Reactive diluents described by Kerr et al. are free radical polymerizable, radiation curable substantially non-volatile liquid monomers or oligomers of up to about 2000 molecular weight selected from monoethylenically unsaturated materials, polyethylenically unsaturated materials, and mixtures thereof. Kerr et al. does not teach adhesion build to polycarbonate, and does not mention the criticality in the selection of the types and amounts of monomers for use with polycarbonates.

Although some solvent based pressure sensitive adhesives have proven to be useful for bonding to polycarbonate surfaces, there has been no teaching that radiation cured pressure sensitive adhesives can bond well to polycarbonate surfaces at elevated temperatures. In fact, it has been observed that the solvent based adhesives decrease in peel adhesion at elevated temperatures. Therefore, there currently exists a need for such pressure sensitive adhesives which maintain adhesion to polycarbonate at elevated temperatures.

It has now been discovered that radiation curable compositions, when radiation cured, yield viscoelastic polymers that are particularly useful as pressure sensitive adhesives that exhibit adhesion build to polycarbonate surfaces after aging at 70°C.

SUMMARY

The invention provides an adhesive composition comprising the radiation-cured polymerization reaction product of starting material comprising:

- (a) from about 50 to about 98 parts by weight of a monomeric acrylic or methacrylic acid ester of a non-tertiary alcohol having from one to about fourteen carbon atoms;
- (b) from about 0 to about 50 parts by weight of a copolymerizable reinforcing monomer;
- (c) greater than about 1 to about 15 parts by weight of a copolymerizing macromonomer; and
- (d) an effective amount of a photoinitiator.

Preferably, the compositions contain 2-10 parts by weight of a copolymerizing macromonomer, and most preferably, the compositions contain 4-9 parts by weight of a copolymerizing macromonomer.

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The compositions can also include portions of components (a) and (b) or portions of (a), (b), and (c) which have been polymerized to a coatable viscosity.

- 5 The invention also provides for a pressure sensitive adhesive, an adhesive article utilizing the adhesive of the present invention, and a method of making the article using the adhesive.

10 The adhesives of the present invention maintain adhesion to polycarbonate when applied to a polycarbonate surface and heat aged for three days at 70°C as compared to comparable aging at room temperature after cure when tested according to Test A described below. Maintaining adhesion, for the purposes of this Application means that there is no loss of adhesion.

- 15 The preferred adhesives exhibit an adhesion build on polycarbonate at 70°C as compared to comparable three day aging at room temperature after cure when tested according to Test A. More preferably, the adhesives exhibit an adhesion build of at least 5% under the above test conditions, and most preferably, at least 10% when tested according to Test A. The preferred adhesives are pressure-sensitive adhesives.

20

DETAILED DESCRIPTION

- The radiation-cured adhesive compositions are essentially 100% solids compositions comprising at least one alkyl acrylate or methacrylate monomer, a copolymerizable reinforcing monomer, and a
- 25 copolymerizable macromonomer.

The copolymerizable macromonomer useful in the practice of this invention is a polymeric moiety having a vinyl group which will copolymerize with the alkyl (meth)acrylate monomer, and if included, the reinforcing monomer. The macromonomer is represented by the

30 general formula



(I)

35

wherein

X is a vinyl group copolymerizable with the alkyl acrylate and reinforcing monomers;

Y is a divalent linking group where n can be zero or one, and

- 40 Z is a monovalent polymeric moiety having a T_g greater than 20°C, a number average molecular weight in the range of about 2,000 to about 30,000, and being essentially unreactive under copolymerization conditions.

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The preferred macromonomer is further defined as having an X group with the general formula



(II)

10

wherein R is a hydrogen atom or a COOH' group and R' is a hydrogen atom or methyl group. The double bond between the carbon atoms provides a moiety capable of copolymerizing with the alkyl acrylate and reinforcing monomers.

15

The preferred macromonomer includes a Z group which has the formula



(III)

25 wherein R² is a hydrogen atom or a lower alkyl group, R³ is a lower alkyl group, n is an integer from 20 to 500, and R⁴ is a monovalent radical selected from the group consisting of

30



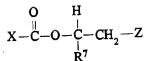
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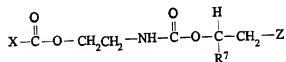
wherein R⁵ is a hydrogen atom or a lower alkyl group, and -CO₂R⁶ wherein R⁶ is a lower alkyl group.

Preferably, the macromonomer has the general formula selected
40 from the group consisting of

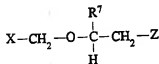
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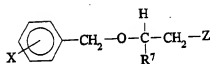
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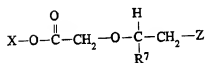
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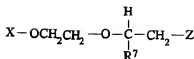


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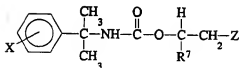


(IX)

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(X)



(XI)

wherein R^7 is a hydrogen atom or a lower alkyl group.

The vinyl-terminated polymeric macromonomers may be prepared by the method disclosed in U.S. Patent Nos. 3,785,116 and 3,842,059 (Milkovich et al.), incorporated herein by reference.

The amount of macromonomer that is useful varies from greater than about 1 to about 15 parts by weight per 100 parts by weight of the total amount by weight of the acrylate monomer, the reinforcing monomer, and the macromonomer. Higher amounts of macromonomer can be used but the cost could be prohibitive. Preferably, the amount of macromonomer is from about 2 parts to about 10 parts and most preferably, from about 4 parts to about 9 parts per 100 parts by weight of the total amount by weight of the acrylate monomer, the reinforcing monomer, and the macromonomer.

The alkyl acrylate or alkyl methacrylate monomers useful in the practice of this invention are monofunctional unsaturated acrylic or methacrylic acid esters of non-tertiary alcohols having from 1 to about 14 carbon atoms with the preferred number of carbon atoms being from about 4 to about 12 carbon atoms. Examples of such monomers include 2-ethylhexyl acrylate, isooctyl acrylate, isononyl acrylate, dodecyl acrylate, decyl acrylate, n-butyl acrylate, hexyl acrylate, and mixtures thereof. Preferred monomers include isooctyl acrylate, butyl acrylate, and mixtures thereof.

The reinforcing co-monomer, if used, is a monomer which if polymerized alone would yield a homopolymer having a higher glass transition temperature, T_g , than the acrylate homopolymer. Examples of such monomers include acrylic acid, methacrylic acid, itaconic acid, acrylamide, substituted acrylamides, N-vinyl pyrrolidone,

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N-vinyl caprolactom, isobornyl acrylate, cyclohexyl acrylate, and acrylonitrile. A preferred co-monomer is acrylic acid.

The compositions also preferably include a photoinitiator. Examples of useful photoinitiators include benzoin ethers such as 5 benzoin methyl ether and benzoin isopropyl ether, substituted acetophenones such as 2,2-diethoxyacetophenone and 2,2-dimethoxy-2-phenylacetophenone, substituted benzoin ethers such as anisoil methyl ether, substituted alpha-ketols such as 2-methyl-2-hydroxypropionophenone, and aromatic sulfonyl chlorides such as 10 2-naphthalene sulfonyl chloride. The photoinitiator is typically used in amounts up to 10 parts per one hundred parts of monomer, and preferably, in amounts from about 0.01 to about 5 parts per hundred parts of monomer.

The adhesive compositions can also include additives as long 15 as they do not adversely affect the curing process or the desired properties of the final product. Useful additives include crosslinking agents, fillers, surfactants, gases, and fibers. The amount and types of fillers are determined by the specific properties desired.

20 Cross-linking agents can be used to improve the internal strength of the adhesive. The cross-linking agent is preferably photoactive. Examples of cross-linking agents include multifunctional acrylates such as 1,6-hexanedioldiacrylate (HDDA), trimethylolpropane triacrylate, and 1,2-ethylene-glycol diacrylate, 25 and substituted triazines such as 2,4-bis(trichloromethyl)-6-(4-methoxyphenyl)-s-triazine and 2,4-bis(trichloromethyl)-6-(3,4-dimethoxyphenyl)-s-triazine. Cross-linking agents can be used in amounts of from 0.01 to about 10 parts per hundred parts of monomer, by weight, and are preferably used in amounts of less than 1 part per 30 hundred parts of monomer.

Tackifiers or tackifying resins may also be added to the adhesive composition to improve adhesion to olefinic surfaces such as polypropylene. The tackifier must be miscible with the acrylate-containing polymer of the adhesive so that macroscopic phase 35 separation does not occur. Useful tackifiers include low molecular weight synthetic hydrocarbon resins, which may be aromatic, aliphatic, or a mixture of aromatic and aliphatic, and low molecular weight rosins and rosin derivatives. Preferred tackifiers include hydrocarbon resins, and especially preferred are hydrogenated 40 hydrocarbon resins polymerized from styrenic-based co-monomers. Preferably, the resins have a weight average molecular weight between about 300 to about 4000, and more preferably, of about 1200 to about 3000. Useful commercially available hydrocarbon-based tackifiers include, among others, those sold by Hercules, Inc. under the

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tradenames Regalrez™, Foral™, Mercotac™, Piccolyte™, and Kristolex™, and those sold by Exxon Chemicals under the tradename Escorez™.

Tackifiers may be used in an amount of from 0 to 50 parts per 100 parts of acrylate. For adhesion to polypropylene, the amounts are preferably in the range of from about 10 to about 40 parts per 100 parts of acrylate, and most preferably in the range of from about 15 to about 30 parts per 100 parts of acrylate.

In a preferred embodiment, for adhesion to polypropylene, the adhesive includes a hydrocarbon tackifier and the reinforcing comonomer is a non-polar monomer such as isobornyl acrylate. A polar comonomer such as acrylic acid may be included as a second comonomer as long as it is used in an amount of less than about 5%.

Suitable fillers include silica, polymeric microspheres, expandable polymeric microspheres, glass bubbles, and fibers. An example of a useful silica is Aerosil R-972 available from Degussa.

Various types of microspheres having an average diameter of 10 to 200 micrometers can be added to impart a foamlike quality to the adhesive. Useful glass microspheres include those disclosed in U.S. Patent Nos. 4,223,067 (Levens), 4,666,771 (Vesley et al.), and 4,612,242 (Vesley et al.).

Polymeric microspheres useful in the adhesive composition include those described in U.S. Patent Nos. 3,615,972, 4,075,138, and 4,287,308. Polymeric microspheres are also commercially available from Kema Nord Plastics under the tradename of "Expancel", and from Matsumoto as F-80ED. The microspheres can be expanded to a specific density of about 0.02-0.36 g/cc and can be added to the adhesive composition in either expanded or unexpanded form. Adding the expanded microspheres will ensure that the microspheres in the adhesive will be substantially surrounded by a thin layer of adhesive.

The composition can also be frothed to form a cellular membrane or cellular pressure sensitive adhesive membrane as taught in U.S. Patent No. 4,415,615 (Esmay et al.), incorporated herein by reference. The cellular pressure sensitive adhesive membrane is prepared by adding appropriate surfactants to a pressure sensitive adhesive composition, frothing the composition by whipping a gas into it, coating the froth onto a support, and polymerizing the composition. If photopolymerization is used, it is preferred to use an inert gas such as carbon dioxide or nitrogen to accomplish the frothing.

The cellular pressure sensitive adhesive membrane can also include hydrocarbon elastomers to increase the internal strength of the membrane. Such hydrocarbon elastomers are disclosed in U.S. Patent No. 5,024,880, herein incorporated by reference. Useful

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elastomers include saturated block copolymers such as styrene-ethylene-butylene-styrene (SEBS). Suitable SEBS and other saturated block copolymers are commercially available from Shell Chemical Company under the tradenames Kraton®G1726, Kraton®G1657, and

5 Kraton®1650.

The viscoelastic polymers are typically prepared by mixing the acrylate monomers with the reinforcing monomers and the photoinitiator, and partially polymerizing in a substantially inert atmosphere under ultraviolet (UV) lamps to form a coatable syrup
10 having a viscosity of about 300 to about 10,000 centipoise. The macromonomer is then added with further photoinitiator, cross-linkers, and other additives, coated onto a web and polymerized with ultraviolet lamps in an inert atmosphere. A sufficiently inert atmosphere can be achieved by sandwiching the adhesive between two
15 films, such as polyester films, that allow most of the UV light to pass through to the adhesive composition, but are substantially impermeable to oxygen. The amount of oxygen tolerable in the curing chamber can be increased by adding oxidizable tin salts such as stannous octoate as disclosed in U.S. Patent No. 4,303,485 (Levens).

20 Alternatively, the macromonomer can be added to the acrylate monomers prior to the formation of the syrup. If desired, other additives are mixed into the syrup before coating and curing.

It is also possible to increase the viscosity by adding thixotropic agents such as silica. The viscosity is typically
25 adjusted to provide the optimum viscosity for the desired coating technique used to apply the composition to the web.

Preferably, the compositions are cured with ultraviolet radiation, and most preferably, some or all of the polymerization is performed using low intensity ultraviolet lamps having an intensity
30 from about 0.1 to about 10 mW/cm². For example, it is possible to polymerize with low intensity lamps to a monomer conversion of about 10 to 90% and then substantially complete the curing with higher intensity lamps. Suitable low intensity lamps include lamps which have about 75% or more of their emission spectra between about
35 280-400 nanometers. Such lamps are commercially available and are sometimes referred to as fluorescent ultraviolet lamps. Examples of high intensity lamps include high and medium pressure mercury arc lamps.

The choice of lamps depends upon the photoinitiator that is
40 used. It is preferred to use lamps which have a large part of the emission spectra around the wavelength at which the initiator is photoactivated.

Although the primary utility for the compositions are in bonding polycarbonate surfaces, the cured compositions are

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viscoelastic in nature and have utility beyond a pressure sensitive adhesive. They can be applied to at least a portion of a surface of suitable flexible or inflexible backing or sheet. For example, it can be applied to a backing to form an adhesive-coated sheet material, especially a tape. As used herein, the term "tape" includes, but is not limited to, those adhesives strips which are single-coated adhesive layers permanently attached to a backing or support, double-coated adhesive strips having flexible supports with an adhesive layer on both sides thereof, and adhesive strips with no support or backing, such being typically though not necessarily releasably attached to a low-adhesion liner, and commonly called "transfer tapes."

The adhesive-coated sheet material may be made by the method comprising the following steps. First, a substrate is provided and coated with an adhesive composition. The adhesive composition comprises: (i) from about 50 to about 98 parts by weight of a monomeric acrylic or methacrylic acid ester of a non-tertiary alcohol having from about 1 to about 14 carbon atoms; (ii) from about 0 to about 50 parts by weight of a copolymerizable reinforcing monomer; (iii) greater than about 1 to about 15 parts by weight of a copolymerizing macromonomer, and (iv) an effective amount of a photoinitiator. Next, the coated substrate is irradiated to cause polymerization of the composition to form an adhesive. The adhesive, after application to a polycarbonate surface, maintains adhesion to the polycarbonate surface after heat aging at 70°C for 72 hours, when tested according to Test A. This general method may be applied to produce any of the adhesives or adhesive-coated sheet materials described above.

The following non-limiting examples serve to further illustrate the invention.

TEST PROCEDURES

90° Peel Adhesion

A sample is prepared by adhering a 15.2 cm x 11.43 cm sheet of pressure sensitive adhesive on a paper release liner to a 15.2 cm x 15.2 cm x 0.05 mm thick aluminum foil which was obtained from A.J. Oster Foils, Inc. of Alliance, Ohio. A 1.27 cm x 15.2 cm strip is cut and adhered to a 5.08 cm x 12.7 cm test panel made of stainless steel, polycarbonate, or polyphenylene oxide. The laminated sample is then rolled with 2 passes of a 2.05 kg roller. For the initial test results (INIT/RT), the sample is left at room temperature (21°C) for 15 to 20 minutes and then tested. For test results after aging (72Hr/RT or 72Hr/70°C) the panel is left at the test temperature

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(21°C or 70°C, respectively) for 72 hours. The sample aged at 70°C is cooled to room temperature (21°C) before testing.

- For thicker samples such as in Examples 30-32 and C15-C18, the sample preparation is the same as above except that the adhesive is applied to the matte-finish side of a 15.2 cm long x 0.137 cm thick strip of anodized aluminum from Lawrence & Frederick, Inc.

To test the sample, the free end of the aluminum strip is clamped in one jaw of an Instron™ Adhesion tester, and the test panel is mounted on a fixture in the other jaw such that the strip would be removed at a 90° peel angle from the panel. The jaws are pulled apart at a rate of 30.48 cm per minute and the force required to pull the adhesive from the panel is reported in Newtons per decimeter (N/dm). The panels used for the testing are:

1. The stainless steel test panel is an 18 gauge 5.08 cm x 12.7 cm panel with a bright annealed finish from Vincent Metals, Inc. in Minneapolis, MN. The panel is prepared by wiping the bright annealed finish side once with a tissue (Kimwipe™, commercially available from Kimberly-Clark), soaked with acetone, and three times with a tissue soaked with heptane. The adhesive is adhered to the bright annealed finish side.

2. The polycarbonate panel is a 5.08 cm x 12.7 cm x 0.48 cm panel with a smooth finish commercially available as Lexan™ from the General Electric Company. The panel is prepared by wiping three times with a tissue soaked with isopropyl alcohol.

3. The polyphenylene oxide panel is made from Noryl™ (poly(2,6-dimethyl-1,4-phenylene oxide)) available from General Electric Co. The panel is 5.08 cm x 12.7 cm x 0.48 cm and was prepared by wiping 3 times with a tissue soaked with isopropyl alcohol.

30

TEST A

- Test A utilizes the 90° Peel Adhesion Test described above to determine the adhesion of an adhesive composition. A sample is made by adhering an adhesive to a polycarbonate panel as described above, aging the panels for 72 hours at 70°C and then testing the sample for 90° Peel Adhesion after the sample has cooled to room temperature. Another sample is made using the same adhesive composition except that after application to a polycarbonate panel, the sample is aged for 72 hours at 21°C. The peel adhesion value at 21°C is subtracted from the peel adhesion value at 70°C and the difference is divided by the peel adhesion value at 21°C. The difference is converted to percent increase or decrease in adhesion and recorded as % Change (% Chg) with "+" being an increase and "-" being a decrease.

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Static Shear

The sample is prepared by adhering a 1.27 cm wide strip of the pressure sensitive adhesive on a paper release liner to the matte finish side of a 0.05 mm thick strip of aluminum foil described above.

For 90° Peel Adhesion, the aluminum strip is then adhered to a stainless steel panel as described above so that a 1.27 cm x 2.54 cm portion of the adhesive is in contact with the panel. The panel is then placed in an oven at 70°C such that the panel is tilted at 2° from the vertical with the adhesive coated strip on the upper surface of the panel. A 500 gram weight is attached to the strip to pull the strip away from the panel and the time required for the strip to pull away from the panel is then recorded. If no failure occurs within 10,000 minutes, the test is discontinued.

Tensile & Elongation

A sample is prepared by die-cutting out a dumbbell-shaped strip of the pressure sensitive adhesive and wrapping each end of the dumbbell with masking tape. The sample has a central portion having a length of 4.13 cm and a width of 0.635 cm between the enlarged portion of the dumbbell. The sample is tested by clamping the taped ends in the jaws of a tensile tester with a recorder (Sintech or equivalent) and the jaws are pulled apart at a speed of 30.48 cm/min. The elongation at break is calculated as the length of the sample at break divided by the original length of the sample, and recorded as "Elong %". The tensile strength is calculated from the breaking tensile and the thickness of the sample tested, and recorded in Newtons/cm² (Tensile N/cm²).

30 Monomer A (MON A)

A methacrylate-terminated polystyrene polymeric monomer was prepared by dissolving 1000 grams of hydroxy terminated polystyrene macromonomer (Macromer 13K PSOH, obtained from Sartomer) in about 1000 grams of about 50°C methyl ethyl ketone. Super-cel" (a filtering aid from Celite" Corp.) was added to the solution with constant stirring. The cloudy mixture was filtered through a Buchner funnel using a Whatman No. 4 filter paper. The clear filtrate was poured into a 5-neck round bottom flask equipped with a mechanical stirrer, thermometer, Soxhlet adaptor with condenser and drying tube, and two stoppers. An additional 200 grams of methyl ethyl ketone were added to the flask. The solution was heated to reflux and 200 milliliters of methyl ethyl ketone were distilled off. The solution was then cooled to 26°C and 20 drops of dibutyl tin dilaurate, 0.2 gram BHT inhibitor, and 23.8 grams of 2-isocyanatoethylmethacrylate

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(obtained from Dow Chemical Company) were added with stirring. The mixture was heated to about 70°C for 19 hours. After cooling to 21°C, the mixture was added slowly to a vigorously stirred beaker of methanol to precipitate the monomer. The precipitate was then suction filtered through a sintered glass funnel and air dried at room temperature with occasional stirring for about 10 days to yield 956 grams of monomer. The monomer had a number average molecular weight of 10,100g (Mn) and a polydispersity of 1.09 (P).

10 Monomer B (MON B)

A polystyrene polymeric monomer was prepared by dissolving 500 grams of Macromer 13K PSOH in about 500 grams of 50°C methyl ethyl ketone. Super-cel™ was added to the warm cloudy solution and the mixture was filtered through a Buchner funnel lined with a Whatman 15 No. 4 filter paper. The clear filtrate was added to a 2000-ml round-bottomed flask equipped with a thermometer, a stopper, mechanical stirrer, soxhlet adaptor, and a condenser with a drying tube. The solution was heated to reflux and 100 ml of methyl ethyl ketone were distilled off. Thereafter, the solution was cooled to 30°C and the following were added with stirring: 10 drops of divinyl tin dilaurate, 0.1 grams BHT inhibitor, and 15.5 grams of m-isopropenyl- α,α -dimethylbenzyl isocyanate, obtained from American Cyanamid Co. Then the mixture was heated to about 70°C for about 18 hours with stirring. After cooling to room temperature or about 21°C, the mixture was slowly added to a beaker containing methanol with 25 vigorous stirring overnight to precipitate the monomer. The precipitate was isolated by suction filtration and allowed to air dry with occasional stirring. (Mn=10,500 and p=1.02)

30 Monomer C (MON C)

A methacrylate-terminated copolystyrene/t-butyl styrene monomer having a molecular weight of about 10,000 was prepared. A dry 5-necked 5-liter flask equipped with a Dean-Stark trap, condenser, addition funnel, thermometer, inlet tube, and mechanical stirrer was 35 charged with 2260 g cyclohexane. The cyclohexane was heated by reflux under argon and 200 ml of cyclohexane were removed by distillation. The cyclohexane was then cooled to about 45°C, and sec-butyllithium (27.8 ml of 1.1 M solution in cyclohexane, 0.031 mole) was added, followed by a solution of styrene (275.5 g) and 40 t-butyl styrene (49.1 g). The monomers were previously purified by passing them through silica gel and then alumina. An exothermic reaction resulted with the maximum temperature reaching 72°C, while cooling with an ice bath. After 1 hour, excess ethylene oxide (passed over sodium hydroxide pellets) was introduced with vigorous

stirring at a reaction temperature of about 40°C. The mixture was quenched with acetic acid (0.031 mole). After cooling to room temperature, the reaction mixture was saturated with dry air and treated with 2-isocyanatoethyl methacrylate (11.2 g, 0.072 mole) and dibutyl tin dilaurate (4 drops) catalyst. At the end of 14 hours the mixture was precipitated into methanol to yield 278 g of the product ($M_n=8450$; $p=1.09$).

Example 1

10 An acrylate syrup was prepared by mixing 90 parts isooctyl acrylate (IOA), 10 parts acrylic acid (AA), and 0.04 parts per hundred parts monomer (pph) of 2,2 dimethoxy-2-phenylacetophenone (Irgacure[®] 651, available from Ciba Geigy Corp.). The mixture was partially polymerized in a nitrogen atmosphere to a coatable
15 viscosity of about 3000 cps by exposing the mixture to a bank of fluorescent lamps having 90% of the emission spectra between 300 and 400 nm with a maximum at 351 nm at an average intensity of about 1 mW/cm², as calculated from reading the total energy measured with a UV Radiometer, Model No. UR365CH1 from E.I.T. (Electronic
20 Instrumentation & Technology, Inc.). A pressure sensitive adhesive composition was prepared by mixing 98 parts of acrylate syrup with 2 parts of Monomer A, 0.10 pph 2,4-bis(trichloromethyl)-6-(4-methoxyphenyl)-s-triazine, and 0.15 pph Irgacure[®] 651. The resulting
25 composition was degassed in a vacuum and knife coated to a thickness of 0.127 mm onto a 0.114 mm thick polyethylene coated Kraft paper. The coated mixture was polymerized in a nitrogen atmosphere by exposing the mixture to an ultraviolet (UV) intensity of about 0.7 mW/cm² to form a pressure sensitive adhesive. The UV radiation
30 was provided by a bank of fluorescent black lamps, which have 90% of the emission spectra between 300 and 400 nm and a maximum at 351 nm, as measured with a Uvimap Radiometer Model No. UM 365L-S from E.I.T. that is spectrally responsive between 300 and 400 nm, with a maximum at 350 nm. The total energy was 300 millijoules/cm², as measured
35 with a UV Integrating Radiometer, Model UR365CH1 from E.I.T. The test sample was first tested for static shear and had a shear value of greater than 10,000 minutes. The resulting pressure sensitive adhesive layer was tested for 90° peel adhesion after room temperature and heat aging according to the 90° Peel Test. The test
40 results are reported in Table 1.

Example 2

A pressure sensitive adhesive was prepared according to the procedure in Example 1 except that 96 parts of acrylate syrup were

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combined with 4 parts of Monomer A. The resulting pressure sensitive adhesive layer was tested for 90° peel adhesion after room temperature and heat aging according to the 90° Peel Test. The test results are reported in Table 1.

5

Example 2A

- A pressure sensitive adhesive was prepared according to the procedure in Example 1 except that the syrup composition was 95 parts of IOA and 5 parts AA, and 4 pph Monomer A were added to the syrup.
- 10 The resulting pressure sensitive adhesive layer was tested for 90° peel adhesion after room temperature and heat aging according to the 90° Peel Test. The test results are reported in Table 1.

Comparative Examples C1-C2

- 15 Pressure sensitive adhesives were prepared as described in Examples 1 (90/10 IOA/AA), and 2A (95/5 IOA/AA) except that Monomer A was not added to the composition. The resulting pressure sensitive adhesive layer was tested for 90° peel adhesion after room temperature and heat aging according to the 90° Peel Test. The test results are reported in Table 1.
- 20

Comparative Example C3

- A pressure sensitive adhesive was prepared as described in Example 1 except that instead of Monomer A, a hydroxy terminated polystyrene (Macromer 13K PSOH, available from Sartomer) was used.
- 25 The monofunctional hydroxy terminated polystyrene had a molecular weight of about 13,000 and was not polymerizable. The resulting pressure sensitive adhesive layer was tested for 90° peel adhesion after room temperature and heat aging according to the 90° Peel Test.
- 30 The test results are reported in Table 1.

TABLE 1 - 90° Peel Adhesion Test Results

Ex	Composition			Polycarbonate - W/Dm				Stainless Steel N/Dm			
	IOA	AA	MON	Init /RT	72HR/ RT	72HR/ 70°C	% Chg	Init /RT	14day /RT	14Day/ 70°C	
1	88.2	9.8	2	--	58	96	+8	79	144	153	
2	86.4	9.6	4	--	68	68	+26	53	107	100	
2A	91.2	4.8	4	--	72	94	+31	53	144	153	
C1	90	10	0	--	83	55	+31	83	133	180	
C2	95	5	0	--	68	94	-19	53	107	100	
C3	88.2	9.8	2*	68	60	55	-39	--	--	--	

* Macromer 13K FSOH used instead of Monomer A.

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The results in Table 1 show that the compositions containing a polystyrene-containing macromonomer increase in adhesion with heat aging on polycarbonate as well as on stainless steel. The compositions of the comparative examples work well on stainless steel, but their peel adhesion decreases with heat on polycarbonate. Moreover, Comparative Example C3 indicated that the monovalent macromonomer must be polymerized with the acrylic monomers.

Example 3

An acrylate syrup was prepared as described in Example 1 except that 97 parts of IOA and 3 parts AA were used to make the syrup. A pressure sensitive adhesive was prepared using 96 parts of syrup and 4 parts of Monomer A as described in Example 1. The test sample was tested for peel adhesion and test results are reported in Table 2.

Example 4

A syrup was prepared by mixing 93.1 parts IOA, 2.9 parts AA, 4.0 parts Monomer A, and 0.04 parts Irgacure™ 651. The mixture was then polymerized to a syrup, 0.10 pph 2,4-bis(trichloromethyl)-6-(4-methoxyphenyl)-s-triazine and 0.15 pph Irgacure™ 651 were mixed into the syrup, and then the mixture was made into a pressure sensitive adhesive as described in Example 1. The test sample was tested for peel adhesion and test results are reported in Table 2.

TABLE 2 - 90° Peel Adhesion Test Results

Ex	Composition			Polycarbonate - N/Dm			
	IOA	AA	Mon A	Init/RT	72Hr/RT	72Hr/70°C	% Chg
3	93.1	2.9	4.0	72	85	92	+ 8
4	93.1	2.9	4.0	74	94	131	+ 40

The results in Table 2 show that mixing Monomer A with the acrylate monomers and forming a syrup exhibit better adhesion build values than mixing Monomer A into an acrylate syrup although both the values exhibited by the compositions of the two compositions were acceptable.

Examples 5-7

Examples 5-7 were prepared according to the procedure of Example 4 except that Monomer A (MON A) was used in Example 5, Monomer B (MON B) was used in Example 6, and Monomer C (MON C) was

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used in Example 7. The test samples were then tested for Peel adhesion and static shear. The Peel Adhesion test results are reported in Table 3. The static shear was measured to be greater than 10,000 minutes.

5

TABLE 3 - 90° Peel Adhesion Test Results

Ex	Composition			Polycarbonate - N/Dm				Noryl™ - N/Dm			
	IOA	AA	MON	Init/ RT	72Hr/ RT	72Hr/ 70°C	% Chg	Init/ RT	72Hr/ RT	72Hr/ 70°C	% Chg
5	91.2	2.8	5	85	105	147	+40	92	122	193	+52
6	91.2	2.8	5	77	99	116	+23	77	94	105	+17
7	91.2	2.8	5	83	99	142	+44	83	123	186	+52

- 20 -

The test results in Table 3 indicate that the compositions of the present invention including macromers containing vinyl groups provide good peel adhesion.

5 Comparative Examples C4-C5

Pressure sensitive adhesive tapes were prepared according to the procedure outlined in Example 4. The ingredients and the percentage of ingredients are reported in Table 4. Both examples utilized 0.08 pph 2,4-bis(trichloromethyl)-6-(4-methoxyphenyl)-s-triazine. The samples were then tested for peel adhesion and results are reported in Table 4.

Examples 8-11

Adhesive compositions were prepared according to the procedure of Example 4 except that the amounts of monomers used are shown in Table 4, and Examples 8 and 10 had 0.02 pph 2,4-bis(trichloromethyl)-6-(4-methoxyphenyl)-s-triazine and Examples 9 and 11 had 0.08 pph 2,4-bis(trichloromethyl)-6-(4-methoxyphenyl)-s-triazine. The samples were then tested for peel adhesion and results are reported in Table 4.

TABLE 4 - 90° Peel Adhesion Test Results							
Ex	Composition			Polycarbonate - N/Dm			
	IOA	AA	Mon A	Init/RT	72Hr/RT	72Hr/70°C	% Chg
25 C4	89	10	1	64	66	53	- 20
C5	96	3	1	81	88	85	- 3
8	88	3	9	46	68	118	+ 74
9	88	3	9	53	59	125	+ 111
10	82	9	9	18	20	31	+ 56
30 11	82	9	9	18	20	39	+ 100

The test results of Table 4 indicate, when viewed in combination with data in Table 1, that adhesive compositions having a macromer content greater than about one percent to about nine percent do build adhesion with heat aging on polycarbonate.

Example 12

An adhesive syrup composition was prepared according to the procedure in Example 4 using 88 parts of IOA, 3 parts of AA, 9 parts of Monomer A, and 0.04 pph of Irgacure®551. An additional 0.15 pph

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of Irgacure[®]651 was added and a pressure sensitive adhesive was prepared and tested as in Example 1. The test sample was tested for peel adhesion and the results are reported in Table 5.

5 Examples 13-14

Pressure sensitive adhesives were prepared and tested as in Example 12 except that in Example 13, 0.05 pph of 2,4-bis(trichloromethyl)-6-(4-methoxyphenyl)-s-triazine was added to the syrup before coating, and in Example 14, 0.15 pph of 1,6-hexanedioldiacrylate was added to the syrup before coating. The test samples were tested for peel adhesion and the results are reported in Table 5.

Comparative Example C6

15 A pressure sensitive adhesive was prepared in accordance with the procedure described in Example 12. The same ingredients were utilized except that no Monomer A was added. This sample was then tested for peel adhesion and the results are reported in Table 5.

20

TABLE 5 - 90° Peel Adhesion Test Results

Ex	Polycarbonate - N/Dm				Noryl [™] N/Dm			
	Init/ RT	72Hr/ RT	72Hr/ 70°C	% Chg	Init/ RT	72Hr/ RT	72Hr/ 70°C	% Chg
12	55	70	110	+ 57	53	85	153	+ 78
13	50	61	110	+ 79	53	81	153	+ 87
14	39	42	85	+ 202	37	50	118	+ 134
25 C6	94	92	81	- 12	81	85	83	- 3

25 The test results in Table 5 indicate that the adhesives of the present invention with or without crosslinking agents exhibit 30 adhesion build after heat aging.

Example 15

An adhesive syrup composition was prepared in Example 4 except that the syrup was made with 88.8 parts IOA, 6.2 parts AA, 5.0 parts 35 of Monomer A, and 0.04 pph Irgacure[®]651. An additional 0.15 pph Irgacure[®]651 and 0.05 pph 2,4-bis(trichloromethyl)-6-(4-methoxyphenyl)-s-triazine were added, and a pressure sensitive adhesive was prepared as described in Example 1. The sample was tested for peel adhesion and the results are shown in Table 6.

40

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Comparative Examples C7-C8

An adhesive composition was prepared by combining 88.8 grams of IOA, 6.2 grams AA, and 5.0 grams Monomer A, 150 grams ethyl acetate, and 0.4 grams of 2,2'-azobis(isobutyronitrile) initiator (available from DuPont Company) in a 1-pint bottle. The bottle was purged with argon, sealed, and tumbled in a water bath at 55°C for 48 hours. The resulting adhesive composition had a solids content of 40% and was diluted to 25% with ethyl acetate for Example C7 and with toluene for Example C8. The resulting composition was coated onto a 0.03 mm thick polyester film and dried to yield a pressure sensitive adhesive having a thickness of 0.11 mm. The test sample was tested for peel adhesion and the results are shown in Table 6.

Comparative Example C9

A pressure sensitive adhesive was prepared as in accordance with the procedure described in Example C4 using 90 parts IOA and 10 parts AA. Monomer A was omitted. This sample was tested for peel adhesion and the test results are reported in Table 6.

TABLE 6 - 90° Peel Adhesion Test Results

Ex	Composition			Polycarbonate - N/Dm		
	IOA	AA	Mon A	Init/RT	72Hr/70°C	% Chg
15	88.8	6.2	5.0	55	66	+ 47
C7	88.8	6.2	5.0	--	116	- 23
C8	88.8	6.2	5.0	--	114	- 17
C9	90	10	0	--	99	- 33

The test results in Table 6 indicate that solution or solvent based adhesives having the same monomeric compositions as the radiation cured adhesives of the invention do not exhibit adhesion build to polycarbonate. Moreover, Example C9 which is a solvent based pressure sensitive adhesive having no macromonomer, exhibits a decrease in adhesion with heat aging.

Examples 16-29 and Comparative Examples C10-C14

Pressure sensitive adhesives were prepared as in Example 4 using the types and amounts of monomers indicated in Table 6. The monomers used are butyl acrylate (BA), isobornyl acrylate (IBNA), cyclohexylacrylate (CHA), 2-phenylethylacrylate (PEA). The compositions for Examples 16-19 included 0.06 pph of 2,4-bis(trichloromethyl)-6-(4-methoxyphenyl)-s-triazine crosslinker and Examples 20-29 included 0.10 pph of this crosslinker. Comparative

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examples C10-C14 were prepared as the corresponding Examples except that no macromonomer was included. The ingredients, the amount of ingredients, and the peel adhesion test results for Examples 16-29 and Comparative Examples C10-C14 are reported in Table 7. The 5 samples were also tested for static shear.

TABLE 7 - 90° Peel Adhesion Test Results

Ex	Composition				Polycarbonate - N/Dm			
	ION	BA	Other/Type	Mon A	Init/RT	72Hr/RT	72Hr/70°C	% Chg
16	70	4	20/BA	6	81	105	166	+58
17	50	4	40/BA	6	88	120	164	+35
18	70	4	20/BA	6*	68	85	127	+49
19	50	4	40/BA	6*	72	101	136	+35
20	40	4	50/BA	6	96	114	164	+44
21	20	4	70/BA	6	120	145	186	+29
22	0	4	90/BA	6	120	129	195	+51
C10**	0	3	97/BA	0	90	186	195	+5
23	77	3	15/IBNA	5	77	94	164	+74
24	62	3	30/IBNA	5	64	79	164	+108
C11	64	3	32/IBNA	0	90	105	107	+2
25	77	3	15/CHA	5	83	110	168	+54
26	62	3	30/CHA	5	83	112	201	+80
C12	65	3	32/CHA	0	94	118	79	-33

TABLE 7 - 90° Peel Adhesion Test Results

Ex	Composition			Polycarbonate - N/Dm				
	IOA	AA	Other/Type	Non A	Init./RT	72Hz/RT	72Hz/70°C	% Chg
27	88	3	3/PEA	3	88	105	147	+40
C13	89	3	8/PEA	0	88	105	83	+71
28	88	3	4/NNDMA	●	92	85	149	+74
C14	88	3	4/NNDMA	0	92	103	70	-32
29**	72	0	20/NNDMA	9	101	105	175	+36

*Instead of Monomer A, an equivalent amount of Chemlink® C4500 (2-polyethyl ethyl acrylate) available from Sartomer Co. was used.

**Samples were cured with the lamps described in Example 1 by exposing the coated mixture to an UV intensity of 1.6 Mw/cm² and a total energy of 285 mJ/cm².

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Upon testing, it was found that the test samples of each of the Examples had static shear values of greater than 10,000 minutes on stainless steel. Moreover, the test data indicate that the compositions of the present invention had superior adhesion build as compared to the compositions of the Comparative Examples.

Example 30

A pressure sensitive adhesive composition having the monomer composition shown in Table 8 was prepared according to the procedure described in Example 4. After the syrup was made, the following were added: 10 pph of hydrophobic silica (Aerosil®R-972 available from Degussa), 8 pph glass bubbles (C15/250 sold by the Minnesota Mining and Manufacturing Co. as Scotchlite® Glass Bubbles), 0.1 pph 1,6-hexanedioldiacrylate, and 0.10 pph of a photoinitiator (Eccacure®KB-1, available from Sartomer Co.). The mixture was degassed and fed into the nip of a knife coater to a thickness of about 1.27 mm between two sheets of transparent, biaxially-oriented polyethylene terephthalate films which had the facing surfaces coated with a silicone release coating. The coated mixture was exposed to a UV intensity of about 1.5 mW/cm² on each side, using fluorescent lamps as described in Example 1 on both sides of the composite. Cooling air was blown on the films during curing. The total energy used on each side was 400 mJ/cm². This total did not include the radiation absorbed by the polyethylene terephthalate films. The sample was then tested for peel adhesion. The test results are reported in Table 8.

Comparative Example C15

Comparative Example C15 was made in accordance with the procedures discussed in Example 30 except that Monomer A was not added. The sample was then tested for peel adhesion. The test results are reported in Table 8.

TABLE 8 - 90° Peel Adhesion Test Results							
Ex	Composition			Polycarbonate - N/Dm			
	IOA	AA	Mon A	Init/RT	72Hr/RT	72Hr/70°C	% Chg
30	92.2	4.8	3	99	142	206	+45
C15	95	5	0	127	162	92	-43

The test results in Table 8 show the feasibility of adding fillers to the adhesive composition while maintaining the elevated temperature adhesion to polycarbonate.

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Example 31 and Comparative Example C16

Pressure sensitive adhesive mixtures for Example 31 and Comparative Example C16 were prepared as in Example 30 and Comparative Example C15, respectively. After degassing the mixture a cellular pressure sensitive adhesive membrane was prepared as follows. The mixture was pumped into a 90 mm frother operating at 300-350 rpm. Concurrently, nitrogen and a 60/40 mixture of Surfactant A*/Surfactant B** (approximately 1-2 parts per one hundred parts of total composition) were fed into the frother. As the frother was continually fed with nitrogen, the frothed mixture was delivered under about 205 kPa pressure to the nip of a knife coater, and cured according to the procedure described in Example 30 to form the cellular pressure sensitive adhesive membrane.

*Surfactant A - $C_8F_{17}SO_2N(C_2H_5)(C_2H_4O)_7CH_3$

**Surfactant B - 50% solids solution of the fluoroaliphatic oligomer of U.S. Patent No. 3,787,351, incorporated herein by reference.

TABLE 9 - 90° Peel Adhesion Test Results

Ex	Composition			Polycarbonate - N/Dm			
	IOA	AA	Mon A	Init/RT	72Hr/RT	72Hr/70°C	% Chg
31	92.2	4.8	3.0	72	81	151	+86
C16	95	5	0	70	123	72	-41

The test results in Table 9 show that elevated temperature adhesion to polycarbonate is not adversely affected when gas is added to provide a cellular foam.

Example 32

A composition was prepared by dissolving 7.8 parts of a styrene-ethylene/butylene-styrene (SEBS) block copolymer (Kraton®G-1657, available from Shell Chemical Company) in 75.8 parts IOA. To this mixture was added 13.4 parts AA, 3 parts MON A, 5.5 pph Aerosil®R-972, 0.46 pph HDDA, and 0.14 pph Escacure®KB-1. After mixing, the mixture was degassed and a cellular pressure sensitive adhesive membrane was prepared according to the procedure described in Example 31. The coated mixture was exposed to an UV intensity of about 1.8 mW/cm² on each side to cure the mixture. The other conditions were maintained as described in Example 30. The total energy on each side was 250 mJ/cm². The sample was then tested for tensile strength, elongation and peel adhesion. The test results are reported in Table 10.

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Comparative Examples C17-C18

Comparative Example C17 was prepared by dissolving 8 parts of SEBS in 78.2 parts of IOA monomer. To this mixture were added 13.8 parts of AA, 0.14 pph Escacure™KB-1, and 6 pph Aerosil™R-972, and a cellular pressure sensitive adhesive membrane was made according to the procedure of Example 32.

Comparative Example C18 was made in accordance with the procedure of Comparative Example C17. The ingredients, the percent ingredient, and the test results for tensile strength, elongation, and peel adhesion are reported in Table 10.

TABLE 10 - Tensile Strength, Elongation, and 90° Peel Adhesion Test Results

Ex	Composition				Physical Properties					Polycarbonate - N/Dm		
	IOA	AA	Non A	SEBS	Thick- ness- mm	Density Kg/M ³	Tensile kPa	Elong %	Init/ RT	72Hr/ RT	72Hr/ 70°C	% Chg
32	75.8	13.4	3	7.8	0.97	753	1565	957	77	94	114	+21
C17	78.2	13.8	0	0	1.02	721	no brk*	---	101	134	74	-44
C18	85	15	0	0	1.04	785	1082	957	83	123	44	-64

* sample did not break

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Examples 33-36

Pressure sensitive adhesive compositions were prepared according to the procedure described in Example 4 except that the monomer composition was 90 parts IOA, 4 parts AA, and 6 parts Monomer A. Tapes were prepared by coating the composition to a thickness of 0.127 mm on a silicone coated release liner. The samples were first exposed to low intensity lamps (0.7 mW/cm²) as described in Example 1, and then to higher intensity lamps (29 mW/cm²) as measured with a Uvimap Radiometer, Model UM365H-S from E.I.T.) for varying times to obtain the total energy for each intensity shown in Table 11. All of the adhesives had static shear values of greater than 10,000 minutes. The samples were monitored for total energy and then tested for peel adhesion. The test results are reported in Table 11.

15

TABLE 11 - 90° Peel Adhesion Test Results						
Ex	Total energy, (mJ/cm ²) at 0.7 mW/cm ²	Total energy, (mJ/cm ²) at 29 mW/cm ²	Polycarbonate - N/Dm			
			Init/RT	72Hr/RT	72Hr/70°C	% Chg
33	124	101 (1 lamp)	66	74	138	+85
34	73	62 (1 lamp)	61	15	77	+85
35	124	403 (4 lamps)	61	72	123	+70
36	73	244 (4 lamps)	57	70	140	+100

20

The test results shown in Table 11 illustrate the feasibility of using a combination of high intensity and low intensity UV radiation which can be used to cure the compositions of the invention.

Examples 37-38

A pressure sensitive adhesive composition was prepared by mixing 84.6 parts IOA, 8.5 parts IBNA, 0.9 parts AA, 6 parts Mon A, and 0.04 parts Irgacure[®]651 in a pint jar. The jar was purged with nitrogen and irradiated with UV black lights to obtain a syrup having a viscosity of about 2900 centipoise. For Example 37, another 0.15 part of Irgacure[®]651 and 0.15 part 2,4-bis(trichloromethyl)-6-(4-methoxyphenyl)-s-triazine were added to 100 parts of syrup and mixed. For Example 38, another 0.15 part of Irgacure[®]651, 0.15 part 2,4-

- 31 -

bis(trichloromethyl)-6-(4-methoxyphenyl)-s-triazine, and 25 parts of Regalrez™6108 tackifier (available from Hercules, Inc.) were added to 100 parts of syrup. After degassing, the syrups were coated to a thickness of 0.127 mm and cured to form pressure sensitive
5 adhesives as described in Example 1 except using an intensity of 2.15 mW/cm², and a total energy of 571 mJ/cm². The adhesives were tested for 90 degree peel adhesion on stainless steel panels, polycarbonate panels, and polypropylene panels according to the above described test procedure. Test results are shown in Table 12.

TABLE 12 - 90° Peel Adhesion Test Results (N/dm)

Ex	Stainless Steel				Polycarbonate				Polypropylene			
	Init/RT	72HR/RT	72HR/70°C		Init/RT	72HR/RT	72HR/70°C		Init/RT	72HR/RT	72HR/70°C	
37	46	61	123		79	77	79		37	33		35
38	63	101	210		90	114	116		72	114		96

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The data in Table 12 show that the addition of a hydrocarbon tackifier improves the adhesion to polypropylene while maintaining good adhesion to polycarbonate.

In summary, novel adhesives, adhesive products, and methods of making adhesive products are described. Although specific embodiments and examples of the present invention have been described herein, it should be borne in mind that these are by way of explanation and illustration and the present invention is not limited thereby. Certainly, modifications which are within the ordinary skill in the art are considered to lie within the scope of this invention as defined in the following claims including all equivalents.

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We Claim:

1. An adhesive composition comprising the radiation-cured polymerization reaction product of starting materials comprising:

- 5 (a) from about 50 to about 98 parts by weight of a monomeric acrylic or methacrylic acid ester of a non-tertiary alcohol having from 1 to about 14 carbon atoms;
- (b) from about 0 to about 50 parts by weight of a copolymerizable reinforcing monomer;
- 10 (c) greater than about 1 to about 15 parts by weight of a copolymerizing macromonomer; and
- (d) an effective amount of a photoinitiator,
- wherein said composition, after application to a polycarbonate surface, maintains adhesion to said polycarbonate surface after heat
- 15 aging at 70°C for 72 hours when tested according to Test A.

2. The adhesive composition of Claim 1, wherein said macromonomer is represented by the following general formula:

20



(I)

25 wherein

X is a vinyl group copolymerizable with said acrylic or methacrylic acid ester and said reinforcing monomer;

Y is a divalent linking group where n can be zero or one; and

30 Z is a monovalent polymeric moiety having a T_g greater than 20°C, a number average molecular weight in the range of about 2,000 to about 30,000, and being essentially unreactive under copolymerization conditions.

35 3. The adhesive composition of Claim 2, wherein said X group of said macromonomer has the general formula:

40



(II)

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wherein R is a hydrogen atom or a COOH group and R' is a hydrogen atom or methyl group.

4. The adhesive composition of Claim 2 or 3, wherein said
5 Z group has the general formula



10

(III)

wherein R² is a hydrogen atom or a lower alkyl group, R³ is a lower
15 alkyl group, n is an integer from 20 to 500, and R⁴ is a monovalent
radical selected from the group consisting of:



20

(IV)

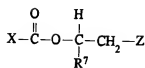
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wherein R⁵ is a hydrogen atom or a lower alkyl group, and -CO₂R⁶,
wherein R⁶ is a lower alkyl group.

5. The adhesive composition of Claim 2, wherein said
30 macromonomer has a general formula selected from the group consisting
of:

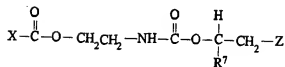
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(V)

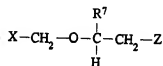
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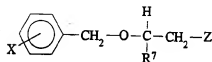
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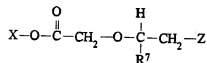
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(VIII)

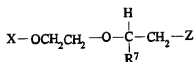
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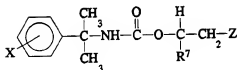
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(X)

or



(XI)

wherein R⁷ is a hydrogen atom or a lower alkyl group.

- 20 6. The adhesive composition of Claim 1, wherein said reinforcing monomer is selected from the group consisting of acrylic acid, methacrylic acid, itaconic acid, acrylamide, substituted acrylamides, N-vinyl pyrrolidone, n-vinyl caprolactam, isobornyl acrylate, cyclohexyl acrylate, and acrylonitrile.

- 25 7. The adhesive composition of Claim 1, wherein said composition exhibits an adhesion build to polycarbonate surfaces after heat aging at 70°C for 72 hours.

- 30 8. The adhesive composition of Claim 1, wherein said composition is a pressure-sensitive adhesive.

9. The adhesive composition of Claim 1, wherein said starting materials further comprise a tackifier that is miscible in
35 said polymerization reaction product.

10. An adhesive-coated sheet material including a backing and an adhesive composition coated on at least a portion of said backing, wherein said adhesive composition is the adhesive composition of one
40 of Claims 1 to 9.

INTERNATIONAL SEARCH REPORT

International Application No.

PCT/US 93/11805

A. CLASSIFICATION OF SUBJECT MATTER
IPC 5 C09J4/06 C09J7/02

According to International Patent Classification (IPC) or to both national classification and IPC

B. FIELDS SEARCHED

Minimum documentation searched (classification system followed by classification symbols)

IPC 5 C09J C09D C08F

Documentation searched other than minimum documentation to the extent that such documents are included in the fields searched

Electronic data base consulted during the international search (name of data base and, where practical, search terms used)

C. DOCUMENTS CONSIDERED TO BE RELEVANT

Category * Citation of document, with indication, where appropriate, of the relevant passages

Relevant to claim No.

P, X	DATABASE WPI Week 9305, Derwent Publications Ltd., London, GB; AN 93-040667 & JP, A, 4 366 103 (SEKISUI CHEM IND) 18 December 1992 see abstract	1-6, 8-10
X	EP, A, 0 187 044 (ATLANTIC RICHFIELD COMPANY) 9 July 1986 cited in the application see the whole document	1-6, 8, 9

☐ Further documents are listed in the continuation of box C.☒ Patent family members are listed in annex.

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Date of the actual completion of the international search

8 March 1994

Date of mailing of the international search report

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Name and mailing address of the ISA

European Patent Office, P.B. 5813 Paternlaan 2
NL - 2280 HH Rijswijk
Tel. (+31-70) 340-2040, Tx. 31 651 epo nl,
Fax (+31-70) 340-2016

Authorized officer

Andriollo, G

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INTERNATIONAL SEARCH REPORT

information on patent family members

Intern. Patent Application No.

PCT/US 93/11805

Patent document cited in search report	Publication date	Patent family member(s)	Publication date
EP-A-0187044	09-07-86	JP-A- 61197618	01-09-86

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